Biosynthesis and Kinetics of Silver Nanoparticles Formation by Reduction using Banana Kepok (Musa balbisiana) Peel Extract

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Biosynthesis and Kinetics of Silver Nanoparticles Formation by Reduction using Banana Kepok (*Musa balbisiana*) Peel Extract

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Biosynthesis and silver nanoparticles formation during the reduction of $AgNO_3$ were carried out by using an aqueous peel extract of banana kepok (*Musa balbisiana*) as a stabilizing agent. The formation of the stable silver nanoparticles with different concentration of $AgNO_3$ has resulted in mostly spherical particles. The Ultraviolet-Visible spectrophotometer, Transmission Electron Microscopy, X-Ray Diffractometer were used to characterize these biosynthesized silver nanoparticles. The spherical shaped nanoparticles were uniformly distributed with the range diameter of 5 to 50 nm and the particles were naturally crystallized with the crystal structure of the face-centered cubic geometry. Additionally, the kinetics of the formation process of silver nanoparticles was observed by the UV-Vis spectrophotometer. Based on the kinetic functions, the reduction process of banana peel extract had a constant formation rate of the autocatalytic process at 4.35×10^{-4}/s.

Keywords: peel extract, banana kapok, silver nanoparticle, kinetic of formation, biosynthesis

INTRODUCTION

Silver Nanoparticles can be of superior value as materials because of their chemical composition, shape, size, and homogeneity to be properly applied. So it encourages the beginning of chemicals research to synthesis nanoparticle material. The nanoparticle is not only discussed on how it is applied but also on how it is synthesized. The synthesis of a nanoparticle can be done in both chemical and physical methods. Synthesis nanoparticle in the physical method has been considered as a more difficult technique and also costly (Vijayakumar et al, 2018). It is can be exemplified as the atomization process used by the wax polymer to give shape to form a polymer powder from molten polymer (Madua et al. 2013). On the other hand, the chemical method is a method that often used in the synthesis of nanoparticles.

However, recent studies have revealed that some chemical methods are harmful due to the use of hazardous chemicals. Noble metal nanoparticles such as gold (Singh et al. 2015), silver (Gudikandula and Maringanti, 2016), and platinum (Mei et al. 2016) have a very broad application for a human. One of the metals which have been widely studied is silver. It is because Silver nanoparticles are a safe and non-toxic inorganic antibacterial agent that was used for several years ago to kill the microorganisms that cause 600 kinds of diseases (Annamalai and Nallamuthu, 2016). Silver nanoparticles also have a steady property and potential applications in various science disciplines, as an antioxidant and a catalyst (Khan et al. 2016), a material that helps improve the performance of the adsorbent (Rengga et al. 2017a), an optical detector and an antimicrobial agent. Based on its applications, the silver nanoparticle has been mostly used as an antimicrobial agent. Synthesizing silver nanoparticles requires a friendly process. Therefore, a method has been developed by using a living organism such as microorganisms, extracts of plants or plant biomass to make nano-particles (Dauthal and Mukhopadhyay, 2016). This method can be considered as an environmentally friendly nanoparticle production as a green synthesis because it can minimize the use of inorganic hazardous materials.

Additionally, biosynthesis is an alternative method that can replace physically and chemically method. Synthesis process by utilizing the living organism is known as biosynthesis (Kuppusamy et al. 2016). Biosynthesis of the nanoparticle can use microorganisms, as well as herbs or plant extracts. Indonesia as a tropical country has many potential plants that contain secondary metabolites compounds (e.g. terpenoids and flavonoids) that can be utilized in the biosynthesis of silver nanoparticles (Raza et al, 2016).

However, a recent research study shows that most of the microorganisms used in the biosynthesis of nanoparticles have a pathogenic impact on other plant or humans (Krithiga and Jayachitra, 2015). Banana peel extract contains antioxidants e.g. polyphenols, catecholamine, carotenoids, eugenol also which can be used as a reducing agent in the synthesis of silver nanoparticles (Agama-Acevedoa et al, 2016 Rengga et al, 2017b).

Silver has higher toxicity against microorganisms, but lower against mammalian and human cells, thus it is relatively safe for the human. However, silver ions have some weakness, such as forming complexes and the effect of ions remains only for a short time. Therefore, it is important to use the silver in its metal form (Ago), which can exhibit antimicrobial function by inducing the production of reactive oxygen (Mohammad 2015). The antibacterial properties of silver can be affected by its particle size. The silver in nano-size has a greater effect as antibacterial agent compared to a bigger size (Raza et al, 2016). The silver nanoparticles also can biosynthesis using banana Kepok peel extract (Haytham and Ibrahim, 2015). They reported that the synthesized silver nanoparticles had an average size of 23 nm. As mentioned previously, the size of the silver nanoparticles may affect their performance as an antibacterial agent. We believed that the size of silver nanoparticles went down smaller than in the literature (Haytham and Ibrahim, 2015). In this study, our aim is to biosynthesize silver nanoparticles using BPPE. It is expected to produce silver nanoparticles with a smaller size compared to the literature.

EXPERIMENT

In this study, $AgNO_3$ was used as the precursor in the synthesis of silver nanoparticles. The four different of concentrations $AgNO_3$ solution were used (i.e. 0.125; 0.1; 0.75; and 0.05 M) to study the effect of concentration variation on the silver nanoparticles synthesis. Each of solution was reacted with BPPE at constant volume as the bio-reduction. The reaction was set at 50°C for 2 hours. To know the kinetics reaction, performed, the reaction would be identified through a change in absorbance value thereof every five minutes for 2 hours. The kinetic reaction or formation of silver nanoparticles was investigated only on the precursor concentration that produced the smallest silver nanoparticles.

Preparation of Banana Kepok Peels Extract (BKPE)

To prepare of bio-reduction, firstly, peels of banana kepok were washed with clean water. Then 100 g of the peels was put in 300 mL of preheated water (i.e. 80 °C) for 30 minutes to get the BKPE. Afterward, the mixture was filtrated using a clean cloth. Insoluble fraction or macromolecules were separated from the liquid (filtrate). The filtrate was a concentrated extract of peels to be used as a reducing agent. The extract was stored in a refrigerator at 4°C. The extract can be used for further testing or diluted in water at a ratio of 1: 100 to be used directly as a reducing agent and stabilizer in the silver nanoparticle synthesis.

Synthesis of Silver Nanoparticles

The source for silver nanoparticles biosynthesis was the $AgNO_3$ solution. The biosynthesis was carried out by preparing 10 mL of peel extract in 1,000 mL of water and reacted with various concentrations of the $AgNO_3$ solution at different concentrations of 0.125; 0.100; 0.075; and 0.050 M.

Characterization of Silver Nanoparticles

The FT-IR (Shimadzu 8201PC) is used to identify the functional groups existing on peels extract. Determination of the size diameter of the nanoparticles was done using a Transmission electron microscopy (TEM) which was carried out by a JEOL microscope (JEM-1400) with the accelerating voltage 80 kV. The size of the particle can be calculated by SCION software. The X-ray powder diffraction (XRD) analyses were performed on (Shimadzu 7000) with radiation Cu Kα at λ=0.15406 nm. The XRD was performed to determine the formation and structure of silver nanoparticles. UV–visible (Uv-Vis) spectrophotometer (Genesys 10UV) was used to measure the absorbance of solution during the biosynthesis process.

Kinetics of Particles Formation

The formation kinetics of silver nanoparticles was determined at the $AgNO_3$ concentration of 0.05 M reacted with 100 mL of BKPE. During the formation reaction of silver nanoparticles, the color was found to be yellow, which indicates the formation of the silver nanoparticles. During the formation of the nanoparticle, the yellow color was more intense due to the increasing concentration of the synthesized nanoparticles. Absorbance recording was done every five minutes during the 2-hour reaction each 10 minute.

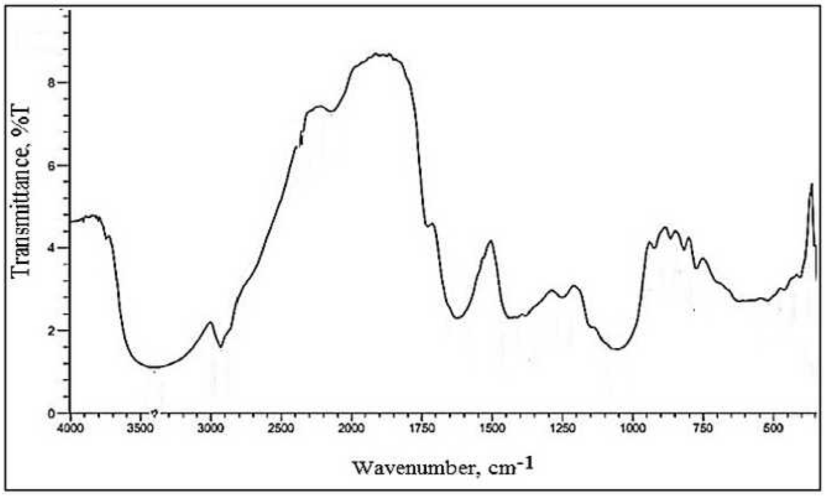

Fig. 1: Spectrum FT-IR of Banana Kepok Peels Extract

Table 1. Functional Groups of Banana Kepok Peels Extract

Group	Boundary specification	Literature wavenumber (cm^{-1})	Banana Kepok Peel Extract Wavenumber (cm^{-1})
C-H	Alkane	2960-2850	2924
C-O-H	Alcohol and phenol	1550-1220	1435
C-H	Alkyl	1380-2870	1381
C-O	Aromatic	1260-1220	1249
C-O	Alcohol phenol	1260-1000	1056
C-H	Alkene	1000-650	925
C-H	Benzene	860-800	817

RESULTS AND DISCUSSIONS

FT-IR test was used to identify the functional groups existing on the BKPE based on the intensity of infrared light that absorbed by the samples. The peel extract as a reducing agent can be identified through the functional group of compounds. The FT-IR spectrum of BKPE (see **Fig. 1**), several groups of compounds contained in BKPE were analyzed. **Table 1** exhibits some compounds that present in the samples of BKPE. The uniqueness of polyphenol compounds has O-H groups and some ring aromatic characterized by group C=C aromatic. A wavenumber of 3402 cm^{-1} indicates the presence of hydroxyl groups specific to alcohol as phenol. Furthermore, C-H groups spread across multiple wavenumbers based on the specific type of bond, e.g. C-H alkane at a wavenumber of 2924 cm^{-1}, alkyl at 1381 cm^{-1} and 926 cm^{-1} for alkenes. The C-H substituted in the benzene lies at a wavenumber of 771 and 817 cm^{-1}. The C-O group of alcohols and phenols at a wavenumber of 1056 cm^{-1}, C-O-H 1435 cm^{-1}, C-O aromatic 1250 cm^{-1}. These results indicate the likely presence of polyphenol compounds (Ibrahim, 2015).

The reducing to form silver nanoparticles by polyphenol compounds can be explained as follow. Initially, polyphenol compounds in solution form radical compounds, which are compounds that have a free electron. Polyphenols in the radical formation will adsorb Ag^+ then the adsorbed Ag^+ ions will undergo in the reduction reaction, which caused delocalization to form Ag^o.

Synthesis of Silver Nanoparticles

The color of a mixture of the $AgNO_3$ solution with BKPE at the beginning of the mixing was white clear. After stirring using a magnetic stirrer for 30 minutes, the colour of the solution appeared to be soft yellow and then became yellow after 1 hour. It happened because the reduction of silver ions, to form silver nanoparticles. The silver nanoparticle was formed when the solution was yellow as a nanoparticle colloid. Such an effects have been reported with natural plant extracts (Logeswari et al. 2015) and with the bark extract of *Cinnamon zeylanicum* (Satishkumar et al., 2009).

X-Ray Diffraction (XRD) of Silver Nanoparticle

The XRD diffractogram result of the silver nanoparticles in **Fig 2.** The XRD diffractogram can be used to identify the form of synthesized Ag. The three highest peaks from XRD thermogram as outlined in **Tabel 2**. Based on the 2-theta results, the silver nanoparticles have been successfully synthesized. It is indicated by the value 2-theta (d(A)) of silver nanoparticles, which are 37.9, 44.1, 64.4, and 77.5 closer to the diffractogram standard of silver in **Table 3.** Calculating the hkl, one can determine the structure of silver nanoparticles of $h^2+k^2+l^2$. The structure of silver nanoparticles can be estimated by using the Debye-Scherrer equation.

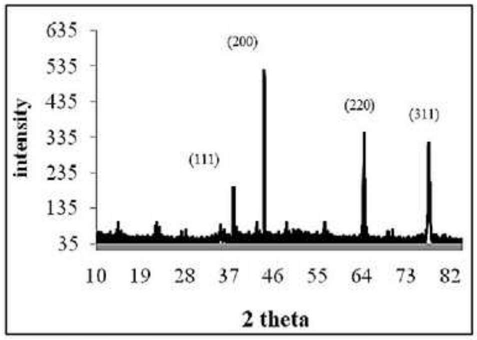

Fig. 2: Difractograms Silver Nano – particles of Silver Nitrate with Banana Kepok Peel Extract

Table 2. The Higher Peak of Nanoparticle Diffractogram

No	Peak Identification		
	Peak No	2θ(°)	Intensity
1	64	44.0962	342
2	74	64.4326	260
3	77	77.5398	251

The list of a possible crystal structure of silver nanoparticles that obtained values of

Table 3. Diffractogram List of Peaks From d – Distance

Peak	Crystal Structure Identification			
2Theta (degree)	D	$1000/d^2$	$h^2+k^2+l^2 = [(1000/d^2)/60.6]$	hkl
37.883	2.373	177.10	3	111
44.096	2.052	237.48	4	200
64.443	1.444	482.30	8	220
77.539	1.230	661.05	11	311

Table 4. Crystal Structure Nanoparticle Silver Determination

Crystal structures	$h^2 + k^2 + l^2$
Simple Cubic (SC)	1,2,3,4,5,6,7,8,9,10,...
Body Centered Cubic (BCC)	2,4,6,8,10,12,14,16,...
Face Centered Cubic (FCC)	3,4,8,11,12,16,19,20,24,27,...

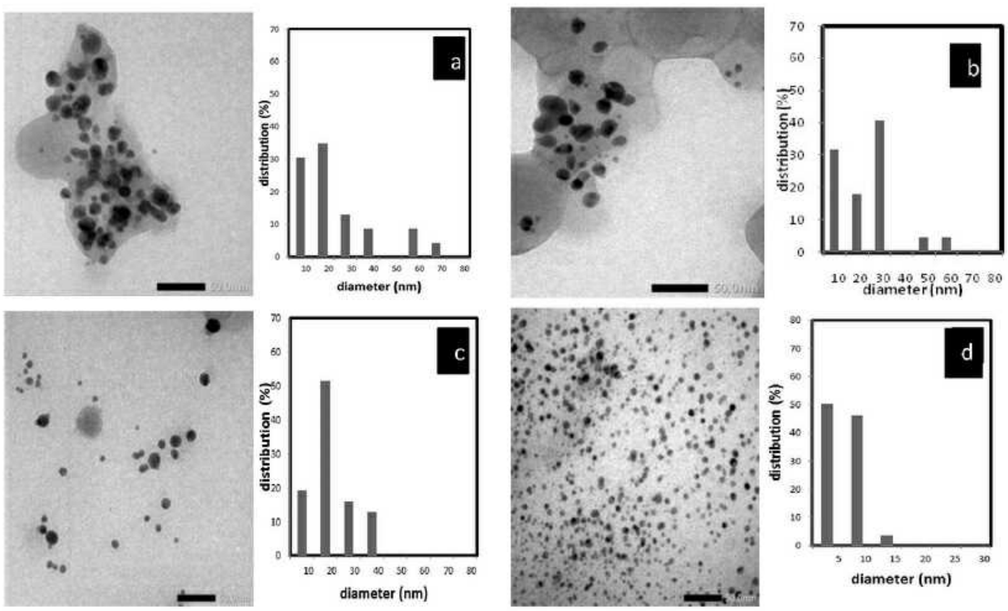

Fig. 3: TEM Data and Size Distribution of Silver Nanoparticles from the Concentration of $AgNO_3$ (a) 0,125 M, (b) 0,100 M (c) 0,075 M (d) 0,050 M

$h^2 + k^2 + l^2$ were 3, 4, 8, and 11 as outlined in **Tabel 4**. Therefore, it can be concluded that the synthesized silver nanoparticles in this study had a structure of Face Centered Cubic (FCC). Hence, it can be concluded that the synthesized silver nanoparticles were in the form of Ag^o.

TEM of Silver Nanoparticles

The TEM images of silver nanoparticles obtained at $AgNO_3$ concentration of 0.125, 0.1, 0.075, 0.05 M, respectively (see **Figs 3a-3d**). The particle size distributions from TEM image are also presented. As shown in the figures, the least concentration of $AgNO_3$ (i.e. 0.005 M) produced a better uniform particle size of silver nanoparticles. Additionally, the average diameter silver nanoparticles obtained at different concentrations of the precursor is shown in **Table 5**. The least concentration of $AgNO_3$ (i.e. 0.005 M) gave the smallest average particle size of silver nanoparticles. The high concentration of $AgNO_3$ used in the synthesis has caused the high number of Ag^+, which led to reduced function of the stabilizer. Hence, it caused larger agglomerations, resulting in the wide distribution of nanoparticles (non-uniformity) and silver nanoparticle size became larger. Conversely, the lower concentration of $AgNO_3$, the smaller agglomeration during the process. Formation nanoparticle for 0.050 M of $AgNO_3$ had the average diameter of 5.48 nm, whereas, 0.125 M of $AgNO_3$ had the average diameter of 12.05 nm.

Table 5. Relation of Concentration $AgNO_3$ to Diameter of Silver Nanoparticle

Concentration of $AgNO_3$ (M)	Diameter (nm)
0.125	12.05
0.100	10.75
0.075	8.44
0.050	5.48

The silver nanoparticles produced using extracts from the peel of banana kepok have a smaller average size than the silver nanoparticles of 2.65 nm and 2.3 nm with the aid of *S. cumini* and *S. tricobatum* extracts, respectively (Logeswari et al. 2015).

The wide particle size distribution of silver nanoparticles has a different ability to perform as an anti-bacterial or a catalyst. Among the different concentrations used in this work, the excellent particle size distribution of silver nanoparticles was obtained by the synthesis using 0.050 M of $AgNO_3$ solution. Furthermore, the silver nanoparticles produced do not occur agglomeration.

The rate of Formation kinetics of autocatalytic process of Ion Nanoparticle Formation

The kinetic analysis of reduction autocatalytic process was carried out of for $AgNO_3$ concentration of 0.05 M. This concentration was selected because the reduction rate was slowest compared to other concentrations, hence the formation of nanoparticles could be controlled and observed. In the reduction reaction process, the mixing reaction was stirred with a magnetic stirrer. Identification was carried out using a UV-Vis spectrometer at λ = 525. The absorption spectrums were recorded every 5 minutes for 200 minutes at a temperature of 50 °C. The data experimental of absorbance to times is shown in **Fig. 4.**

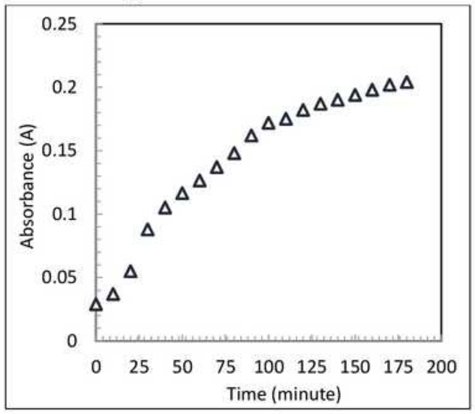

Fig. 4: The Absorbance of Formation of Nanoparticle to time

To calculate the kinetics quantitative functions that describe the reduction reaction, the experimental absorbance data was then converted into ln (a/(1-a)) (where a = A_t/A_∞, and A_t and A_∞, in consecutive, are respectively the maximum absorbance at t and ∞) which changes with time. Autocatalytic process rate constant (ka) can be determined from the slope of curve ln (a / (1-a)) vs t [12], as shown in **Fig. 5**. The rate constant (ka) of reduction reaction of silver ions was found to be 0.000435 /s. This result is similar to the formation and stabilization result of noble metal nanoparticles (Papp et al, 2007).

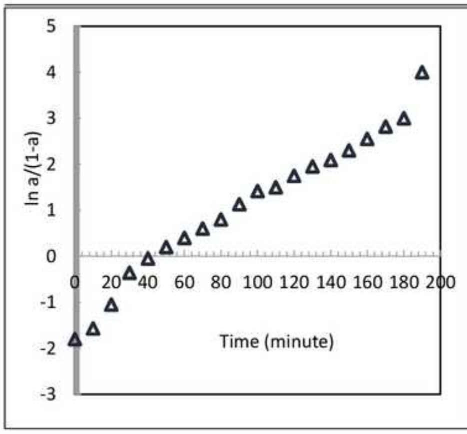

Fig. 5: Function Graphs ln a/(l-a) of the Time

CONCLUSION

1. The silver nanoparticles can be biosynthesized by the reduction reaction using Banana Kepok Peel Extract (*Musa balbisiana*)
2. In the formation of silver nanoparticles, the lower the concentration of the $AgNO_3$ precursor, the less agglomeration and the smallest nanopartel size.
3. The smallest average size of silver nanoparticles (i.e. 5.48 nm) was obtained from the synthesis using $AgNO_3$ precursor concentration of 0.05 M, with a constant rate of formation is 0.000435/s.

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